

# Regio- and Stereochemical Aspects of the Palladium-Catalyzed Reactions of Silanes

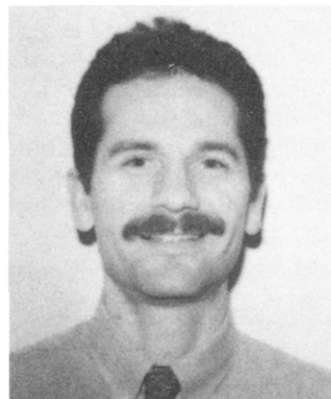
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## I. Introduction

Organosilicon reagents have become major tools in organic synthesis, holding particular importance as protecting groups and regio- and stereochemical directing groups. Over the past 20 years, a wide range of scattered reports have provided evidence that unique, stereospecific chemical transformations of silanes can be carried out with homogeneous Pd(II) and Pd(0) complexes. These reagents hold definite potential to augment the synthetic applicability of a wide range of organosilicon reagents. However, until recently, investigations of the reactions of palladium complexes with both carbo- and polysilanes have generally been of a survey nature and few systematic or mechanistic investigations of the influence of the molecular structure of the palladium complexes on the silane products and their yields have been reported. In addition, investigations of the regio- and stereochemical consequences of reaction conditions and the stereoelectronic nature of the substrate have been of limited scope. Progress has been made, however, in the development of palladium

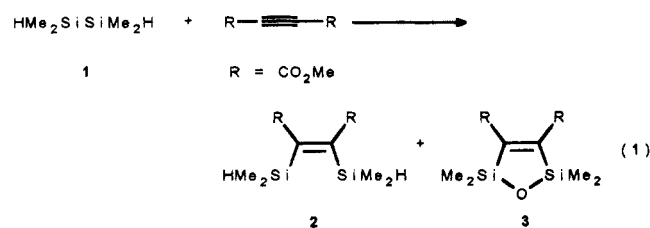
catalysts that operate effectively at room temperature producing products in high yield with well-defined regio- and stereochemistries. These catalysts now provide facile access to a wide variety of functionally activated structures for synthesis. The current review attempts to provide a comprehensive survey of the regio- and stereochemical data on these homogeneous reactions of silanes with palladium complexes. Recent advances are highlighted in such a manner as to stimulate new synthetic and mechanistic work aimed at the stereoelectronic control of these reactions. The scope of this review will involve only those reactions in which a silicon-silicon bond or carbon-silicon bond is cleaved or formed but will not cover the reactions of siloxanes with palladium catalysts or the formation of trimethylenemethane intermediates from acetoxy substituted allylsilanes, an area investigated and reviewed comprehensively by Trost.<sup>1</sup> The synthetic applications of the reactions of silanes with palladium catalysts have been partially reviewed elsewhere.<sup>2</sup>

## II. Palladium-Catalyzed Addition Reactions of Disilanes

### A. Addition Reactions with Acetylenes and Diacetylenes

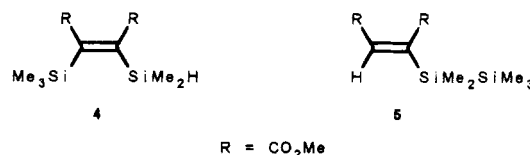
The calculated heat of reaction for the formation of disilylalkenes from substituted disilanes and acetylenes is ca. -40 kcal/mol. This suggests that high-yield double silylation reactions should be feasible even with peralkylated disilanes if appropriate catalysts and kinetically favorable reaction pathways are developed. The transformation is particularly attractive since two silicon-carbon bonds are formed simultaneously. After significant effort, this goal has been achieved, and within the last five years been demonstrated to be feasible even in room temperature reactions (*vide infra*).

The first example of the double silylation of an acetylene using a disilane and a soluble palladium catalyst was reported in 1975. On the basis of their earlier work in which acetylenes were silylated in the disproportionation reactions of disilanes catalyzed by platinum and nickel complexes, Kumada, et al.<sup>3</sup> explored the reaction of *sym*-tetramethyldisilane with acetylenes using soluble Pd(II) catalysts. The reaction of *sym*-tetramethyldisilane (1) with dimethyl acetylenedicarboxylate in benzene at reflux using PdCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub> (0.04 mol %) was found to give a 40% yield of dimethyl  $\alpha,\alpha'$ -bis(dimethylsilyl)maleate (2) as shown in eq 1.

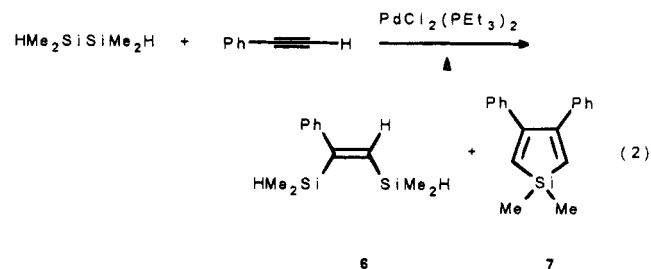


The cyclic disiloxane hydrolysis product 3 was also found in low yields and conversion of 2 to 3 with

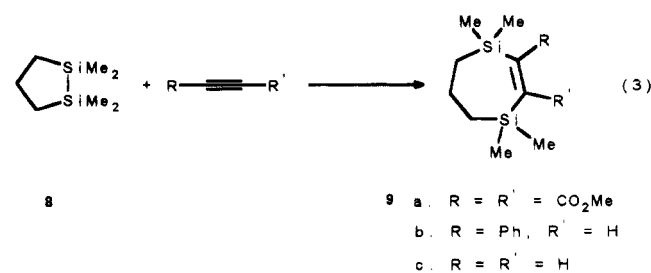
water and PdCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub> served as proof of the (*Z*) stereochemistry of the double silylation product. The reaction of pentamethyldisilane with dimethyl acetylenedicarboxylate under similar conditions gave the corresponding dimethyl  $\alpha$ -(trimethylsilyl)- $\alpha'$ -(dimethylsilyl)maleate (4, 43%) as well as 7% of the hydrosilylation product dimethyl  $\alpha$ -(pentamethyldisilyl)maleate (5). With PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> the yield of 2



decreased to 20% while that of 4 increased slightly. Hexamethyldisilane failed to react under the conditions employed. However, increased temperature and/or longer reaction times can result in low yields of bis(trimethylsilyl)maleate, *vide infra*. The course of the double silylation reaction was also found to be influenced by the nature of the acetylene used. While  $\alpha,\beta$ -bis(dimethylsilyl)styrene (6) was indeed formed in 25% yield when phenylacetylene was used, 1,1-dimethyl-3,4-diphenyl-1-silacyclopentadiene (7) was the major product (eq 2).

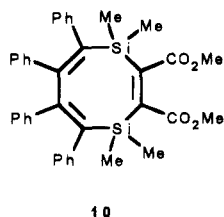


Sakurai et al.<sup>4</sup> also found that the addition of disilanes to acetylenes was catalyzed by Pd(II) complexes. When 1,1,2,2-tetramethyl-1,2-disilacyclopentane (8) was heated in benzene for 3 h with dimethyl acetylenedicarboxylate, phenylacetylene, or acetylene, the substituted 1,1,4,4-tetramethyl-1,4-disilacyclohept-2-enes (9a-c) were formed in yields varying from 53 to 85%.



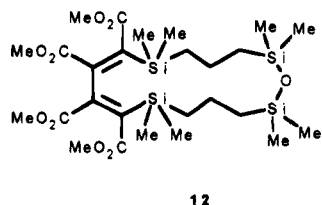
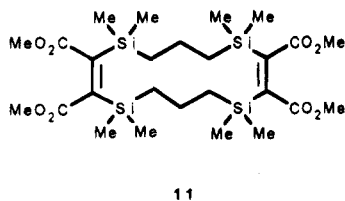
The reaction of hexamethyldisilane with dimethyl acetylenedicarboxylate gave only 3.4% of the double silylation product, under the same conditions, after 23 h. The rapid reaction of the cyclic disilane compared to hexamethyldisilane was attributed to the higher energy of the highest occupied molecular orbital (HOMO) of the ring-strained cyclic disilane. Once again (*Z*) stereochemistry was observed. 1,1,2,2-Tetramethyl-3,4,5,6-tetraphenyl-1,2-disilacyclohexa-

diene also reacted with dimethyl acetylenedicarboxylate to give the cyclic addition product (**10**) in good yield.



Other soluble Pd(II) complexes such as PdCl<sub>2</sub>-(PhCN)<sub>2</sub>, [(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)PdCl]<sub>2</sub>, and PdCl<sub>2</sub>(PEt<sub>2</sub>)<sub>2</sub> catalyze the double silylation reactions, as does the Pd(0) complex Pd(PPh<sub>3</sub>)<sub>4</sub>. The effectiveness of the palladium(0) complex indicates that the Pd(II) catalysts may first be reduced to Pd(0) in these reactions. The formation of 1,4-dichloro-1,4-disilaoctamethylbutane from the reaction of 1 equiv of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> with octamethyl-1,2-disilacyclobutane<sup>5</sup> also provides circumstantial evidence that Pd(II) complexes can be reduced to a coordinatively unsaturated Pd(0) species in the presence of disilanes.

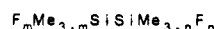
While the course of the double silylation reaction is similar with each of these palladium catalysts, often there are slight variations and different byproducts. For example, when the catalyst PdCl<sub>2</sub>(PhCN)<sub>2</sub> is used in the reaction of 1,1,2,2-tetramethyl-1,2-disilacyclopentane (**8**) with dimethyl acetylenedicarboxylate, the two cyclic structures **11** (benzene, reflux) and **12** (room temperature) are formed as byproducts in low yields. These products were not observed with PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.



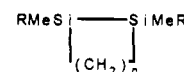
It should be noted that in some cases pentamethyldisilylacetylenes can be reacted with Pd(PPh<sub>3</sub>)<sub>4</sub> at 100 °C, without cleavage of the silicon-silicon bond, as reported by Ishikawa et al.<sup>6</sup> in their investigations of the palladium-catalyzed synthesis of silyl-substituted enynes. Horn et al.<sup>7</sup> have also shown that silicon-silicon bond cleavage does not occur in the Heck reaction of pentamethyldisilylacetylene and heptamethyltrisilylacetylene with various aromatic halides catalyzed by PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> or Pd(PPh<sub>3</sub>)<sub>4</sub> and CuI.

The addition of open chain fluorodisilanes **13** and cyclic fluorodisilanes **14** to the acetylenes **15** also

proceeds readily at 100 °C with either PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> or Pd(PPh<sub>3</sub>)<sub>4</sub> catalysts<sup>8</sup> and seems to be assisted by the electron withdrawing property of the fluorine substituents.



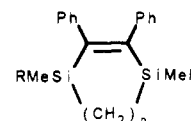
- 13**
- a. m = n = 2
  - b. m = n = 1
  - c. m = 2, n = 0
  - d. m = 1, n = 0



- 14**
- a. n = 3, R = Me
  - b. n = 4, R = F



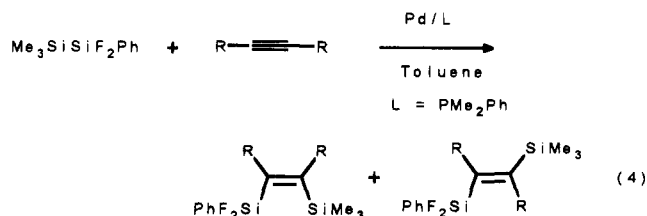
- 15**
- a. R = R' = Ph
  - b. R = Ph, R' = H
  - c. R = R' = Et



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Interestingly, the reaction of the non-fluorinated tetramethyl-1,2-disilacyclopentane (**14a**) with diphenylacetylene (**15a**) was reported to proceed in 78% yield under the conditions used for the fluorinated disilanes. However, Sakurai<sup>4</sup> reported no reaction for the same pair at 80 °C. Not only was the double silylation reaction shown to give the (*Z*) isomers in all cases except where subsequent isomerization of the initially formed (*Z*) isomer occurred, but the reaction was also shown to be stereospecific at both silicon atoms. Thus the reactions of *cis*- and *trans*-**14b** with diphenylacetylene catalyzed by a chiral phosphine-palladium complex gave the (*Si*)-*cis*- and (*Si*)-*trans*-addition product **16** respectively. Since the (*Si*)-*trans* product was found to be optically active, it was assumed that the reaction proceeded stereospecifically with at least partial retention of configuration at both silicon atoms. The (*Si*)-*cis* product, a meso compound, was found to be optically inactive, as expected. A mechanism involving oxidative addition of the silicon-silicon bond to a low-valent palladium phosphine complex, followed by formation of a disilylpalladium(II) intermediate which subsequently adds to the acetylene, was postulated to account for the experimental observations.

Recently Ozawa and Hayashi have reported that a wide variety of acetylenes can be double silylated with Me<sub>3</sub>SiSiF<sub>2</sub>Ph in the presence of [Pd(η<sup>3</sup>-allyl)Cl]<sub>2</sub> and a basic phosphine ligand such as PMe<sub>2</sub>Ph.<sup>9</sup> The highly reactive catalyst system coupled with the unsymmetrically substituted disilane typically gives yields of 95% or higher as shown in eq 4. The

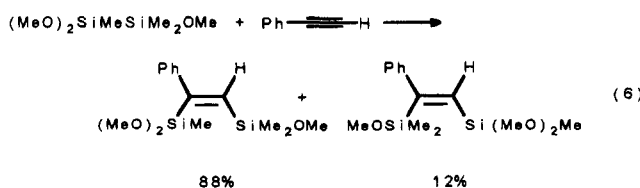
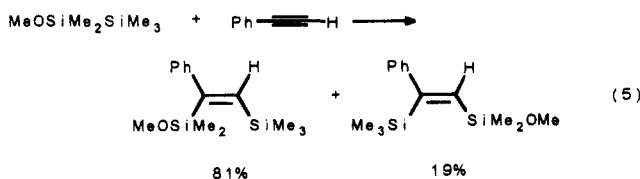


reaction of acetylene itself occurs at room temperature, while temperatures in the range of 40–60 °C are used for alkyl- and phenyl-substituted acetylenes. There is a high selectivity for the (*Z*) isomer (87:1 to 99:1). Internal acetylenes bearing alkyl substituents also give excellent yields.

The additions of 1,1,2,2-tetrachlorodisilane and 1,2-dichlorodisilane to acetylene also proceed smoothly with  $\text{Pd}(\text{PPh}_3)_4$  [1–2 mol %] in toluene or xylene at temperatures between 80 and 130 °C. Yields are in the range of 78–96%.<sup>10</sup> Additional substitution of chlorine for alkyl substituents increases the reactivity of the disilanes toward addition. In a direct competition between 1,2-dichlorotetramethyldisilane and 1,1,2,2-tetrachlorodimethyldisilane, the dichlorodisilane did not react until most of the tetrachlorosilane had reacted. A similar reactivity is seen in the double silylation of 1,3-butadiene, *vide infra*. The unsymmetrical chlorodisilanes such as 1,1,2-trichlorodisilane and chloropentamethyldisilane give lower yields of the 1:1 adducts due to concurrent disproportionation of the disilane to give polysilanes and dimethyldichlorodisilane. Use of  $\text{PdCl}_2(\text{PPh}_3)_2$  as the catalyst resulted in lower yields of the double silylation product. These addition reactions of chlorodisilanes with acetylenes have also been explored by the Toshiba Silicone Company.<sup>11</sup>

A variety of methoxy-substituted disilanes such as 1,2-dimethoxytetramethyldisilane and 1,1,2,2-tetramethoxydimethyldisilane have been successfully added to phenylacetylene with either  $\text{PdCl}_2(\text{PPh}_3)_2$  or  $\text{Pd}(\text{PPh}_3)_4$ ,<sup>12</sup> further illustrating the generality of this double silylation reaction.

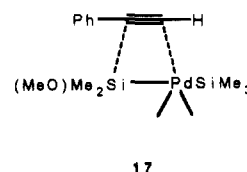
Once again the reaction was shown to specifically yield the (*Z*) stereochemistry products. The Pd(0) complex gave higher yields than the Pd(II) catalysts. It was also noted in this same investigation that hexamethyldisilane gives the double silylation products in low yield. When the unsymmetrical 1-methoxy-pentamethyldisilane and 1,1,2-trimethoxy-trimethyldisilane were added to phenylacetylene, both possible regioisomers ( $\alpha$  and  $\beta$ ) were formed, although the  $\alpha$  regioisomer predominated in both cases (eqs 5 and 6). Addition of the silyl moiety bearing



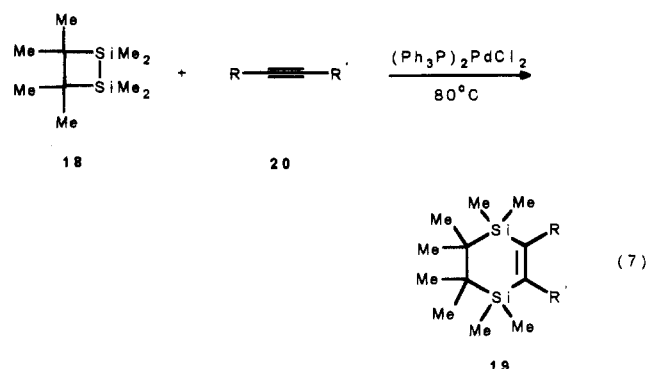
the most methoxy groups to the  $\alpha$  carbon is favored. The isomerization of the (*Z*) alkene products was catalyzed most effectively by the Pd(0) and Pd(II) complexes in the presence of the starting disilane. It was later shown that the same methoxydisilanes would form 1:1 adducts with 1-hexyne, (trimethylsilyl)acetylene, and even acetylene, in 12–76% yields. The double silylation reactions of acetylene were carried out by bubbling acetylene through a toluene or xylene solution containing 1,2-dimethoxytetramethyldisilane or 1,1,2,2-tetramethoxydimethyldisi-

lane at 110 °C. For all of these additions, higher reaction temperatures in general gave higher yields.

The observed regiochemistry of the addition was explained mechanistically by the addition of a disilylpalladium species (formed by the oxidative addition of the methoxydisilane to the Pd(0) complex) to the acetylene substrate in such a manner that the more electron-rich carbon forms the  $\sigma$  bond to the palladium metal (17).

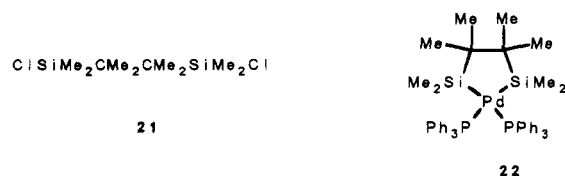


Several mechanistic details of the addition reactions of disilanes with acetylenes were clarified in an investigation of the reaction of octamethyl-1,2-disilacyclobutane with acetylenes, in the presence of Pd(II) catalysts, carried out by Seyferth et al.<sup>5</sup> The strained cyclodisilane **18** was found to form the 1,4-disilacyclohexenes **19** when reacted with terminal acetylenes **20** (57–100% yields).

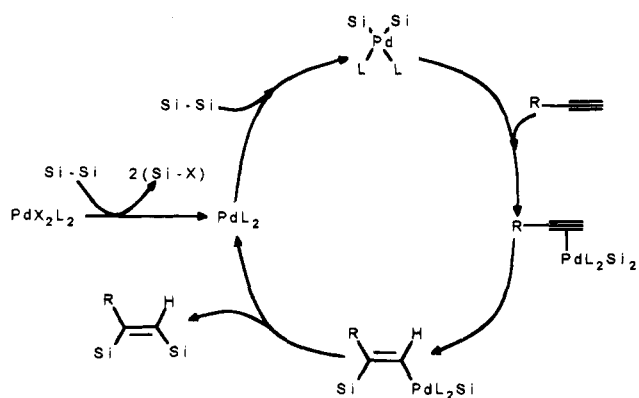


R, R'	Yield (%)	R, R'	Yield (%)
Ph, H	73	Me <sub>3</sub> C, H	96
H, H	57	Me, H	91
H, CO <sub>2</sub> Me	92	MeO <sub>2</sub> C, MeO <sub>2</sub> C	99
n-C <sub>5</sub> H <sub>11</sub> , H	83	Me, C(O)Me	100

When 1 equiv of  $\text{PdCl}_2(\text{PPh}_3)_2$  was reacted with **18**, the chlorosilane **21** was formed along with the palladium species **22**. This suggests that the original Pd(II) catalyst was reduced to a coordinatively unsaturated Pd(0) species that then inserted into the silicon–silicon bond of **18**. The palladium species **22** was shown to react stoichiometrically with phenylacetylene to give the cyclic adduct **19**, the same product obtained from the catalytic reaction.



## Scheme 1

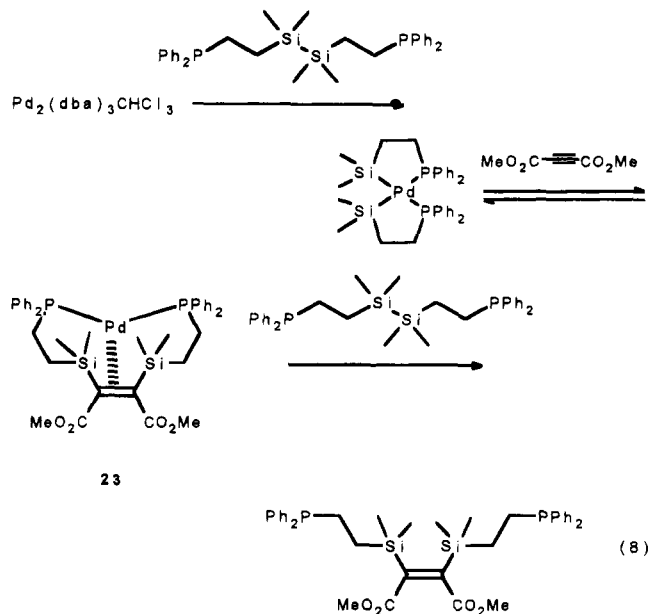


The disilylpalladium compound **22** is therefore a probable intermediate in the catalytic reaction. With this mechanistic information, Scheme 1 provides a viable unifying mechanism for the double silylation reactions of disilanes with acetylenes. The steps included are (1) formation of a Pd(0) catalyst (possibly coordinatively unsaturated), (2) oxidative addition of the disilane to this species, (3) formation of a  $\pi$  complex with the acetylene, (4) insertion of the acetylene into one of the palladium-silicon bonds, and (5) reductive elimination of the disilylalkene product.

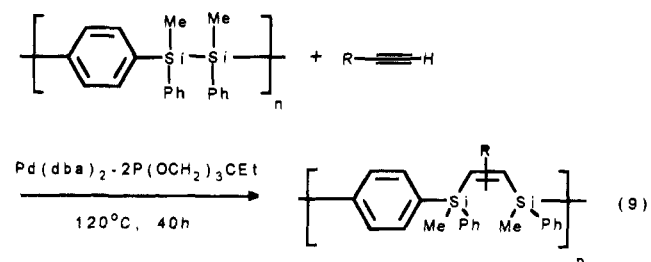
In a reaction analogous to eq 7, 1,4-disilacyclohexa-2,5-dienes were formed by the palladium complex-catalyzed addition of 1,1,2,2-tetramethyl-3,4-diphenyl-1,2-disilacyclobut-3-ene or 1,1,2,2-tetramethyl-3-phenyl-4-trimethylsilyl-1,2-disilacyclobut-3-ene to diphenylacetylene or phenyl(trimethylsilyl)acetylene. The yields of the 1,4-disilacyclohexa-2,5-dienes ranged from 28 to 71% using a wide variety of palladium complexes including  $\text{PdCl}_2(\text{PPh}_3)_2$ ,  $\text{PdCl}_2(\text{PET}_3)_2$ ,  $\text{PdCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ ,  $\text{PdCl}_2(\text{PhCN})_2$ ,  $\text{Pd}(\text{PPh}_3)_4$ , and Pd on charcoal.<sup>13</sup>

The mechanisms postulated for the double silylation of acetylenes propose the involvement of bis-silyl palladium complexes. Similar complexes have been suggested as intermediates in the double silylation reactions of alkenes and in hydrosilylation reactions. Several palladium complexes containing chlorinated silane ligands had been isolated<sup>14</sup> but were highly reactive and unstable in air. A series of palladium complexes containing simple silane ligands [(dcpe)- $\text{Pd}(\text{SiHRMe})_2$  and (dcpe)- $\text{Pd}(\text{SiHRPh})_2$ ] have now been isolated.<sup>15</sup> All are stable in air and are stable to brief heating at 120 °C. The X-ray crystal structure of (dcpe)- $\text{Pd}(\text{SiHMe}_2)_2$  was determined. These complexes react cleanly with dimethyl acetylenedicarboxylate at 25 °C to give *cis*-bis(dimethylsilyl)-maleate, thus strongly supporting the mechanism of Scheme 1. Recently a disilane containing two tethering phosphine groups was utilized to stabilize the intermediate palladium-acetylene *cis*-adduct (**23**). The phosphine tethers acted to stabilize the palladium adduct, making its isolation and characterization possible.<sup>16</sup>

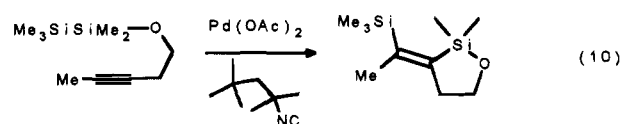
New more highly reactive palladium catalysts have been developed which efficiently catalyze the addition



of simple aryl- and alkyl-substituted disilanes to acetylenes and avoid the general necessity of utilizing disilanes bearing electron-withdrawing groups. Thus  $\text{Pd}(\text{dba})_2-2\text{P}(\text{OCH}_2)_3\text{CEt}$  is an efficient catalyst for the insertion of acetylenes into hexamethyldisilane.<sup>17</sup> The reaction with phenylacetylene proceeds readily at 120 °C to give (*Z*)-1,2-bis(trimethylsilyl)-1-phenylethene in 91% yield. With the conventional catalysts described earlier, the yields are typically below 10%. A unique application of this reaction is the insertion of acetylenes into the SiSi bonds of poly-(disilanylene)phenylene (see eq 9), poly(disilanylene)-ethylene and even poly(dimethylsilylene). It was also shown that this catalyst could be used with 1,7-octadiyne to cross-link poly(disilanylene)phenylene.



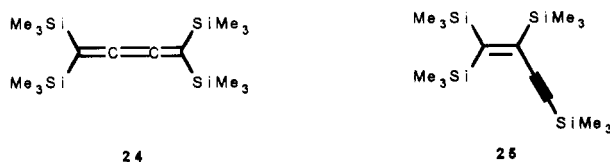
Palladium(II)acetate-*tert*-alkyl isocyanide (excess) also catalyzes the addition of simple alkyldisilanes to acetylenes.<sup>18</sup> Hexamethyldisilane reacts with terminal acetylenes to yield the double silylation products in yields between 80 and 98%. The addition is predominantly *cis* to give the (*Z*) product (*Z/E* ratio > 95:5). Aryl and alkyl terminal acetylenes react, but internal acetylenes are unreactive unless the disilane and acetylene are tethered together by a two- or three-atom tether to force an intramolecular double silylation (eq 10). Addition of 2 equiv of



phenylacetylene to octamethyltrisilane was also ef-

efficient. The same catalyst system has been shown to be effective for the silastannylation of 1-alkoxyalkynes to give 1-alkoxy-1-silyl-2-stannylalkenes which can be converted to acysilanes.<sup>19</sup>

The only known example of the double silylation of a diacetylene is the reaction of 1,4-bis(trimethylsilyl)butadiyne with chlorodisilanes to yield 1,1,4,4-tetrakis(trimethylsilyl)butatriene (**24**) and 1,1,2,4-tetrakis(trimethylsilyl)-1-buten-3-yne (**25**) (after methylation).<sup>20</sup> The combined yields of **24** and **25** were as high as 81%, with 1,4 addition (**24**) being favored by increased chlorine substitution on the disilane. The full report of this addition reaction

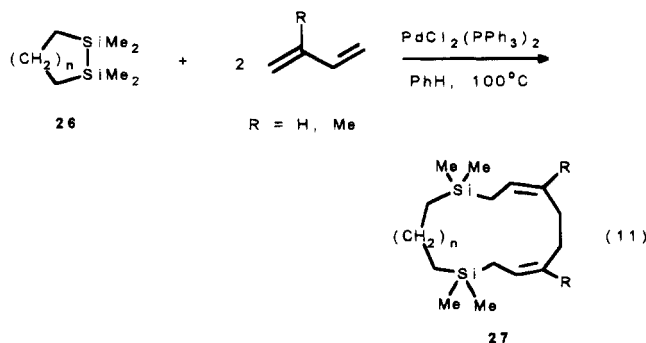


showed that **24** remained the major product over a wide range of  $\text{PdCl}_2(\text{PR}_3)_2$  except for  $\text{R} = \text{Et}$  and  $\text{R} = \text{CH}_2\text{Ph}$  which gave 72 and 74% yields of **25** respectively.<sup>21</sup> Less bulky phosphine ligands were generally more reactive. Some data indicated that the addition was *cis*. Hexamethyldisilane gave only a small amount of the 1,2-addition product **25** and hexachlorodisilane underwent only polysilane formation.

The best combined addition product yields were obtained with the Pd(II) catalysts  $\text{PdCl}_2(\text{PET}_3)_2$  and  $\text{PdCl}_2[\text{P}(\text{CH}_2\text{Ph})_3]_2$ . The reaction forming the 1,2-addition product, **25**, was found to proceed in a *cis* fashion, as seen for the addition reactions of disilanes with simple acetylenes. The mixtures of (*E*) and (*Z*) **25** were generated by thermal isomerization during their isolation by gas chromatography.

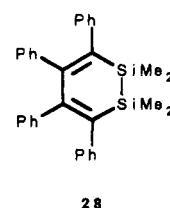
## B. Addition Reactions with Dienes and Allenes

The reactions of disilanes with dienes, catalyzed by palladium complexes, result in both 1:1 and 1:2 addition products. The first report of such disilane addition reactions involved the reaction of strained cyclic disilanes **26** with excess butadiene or isoprene in benzene at 100 °C in the presence of  $\text{PdCl}_2(\text{PPh}_3)_2$ .<sup>22</sup> The 1:2 macrocyclic addition products **27** were isolated exclusively.



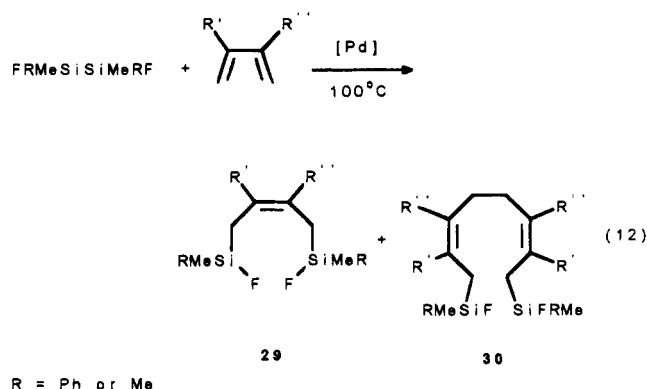
The reactions of 1,1,2,2-tetramethyl-1,2-disilacyclopentane with butadiene and isoprene were especially

efficient (83 and 76% yields, respectively). Interestingly, only the head-to-head dimer structure was observed when isoprene was used. 1,1,2,2-Tetramethyl-3,4,5,6-tetraphenyl-1,2-disilacyclohexadiene (**28**) was also found to add readily to 1,3-butadiene (86%).



Linear disilanes such as hexamethyldisilane and 1,2-dichlorotetramethyldisilane were found to add to isoprene to give 1:2 head-to-head addition products, although in low yield (5–14%). While a variety of Pd(II) complexes were effective catalysts, Pd(0) catalysts were reported to be rather ineffective. A later report from the Toshiba Silicone Company showed that Pd(0) catalysts could also be effective for the addition to dienes when used at 130 °C in benzene.<sup>23</sup> When  $\text{Pd}(\text{PPh}_3)_4$  was used for the addition of hexamethyldisilane to butadiene, the 1:2 adducts were formed in 76% yield. The most effective of the Pd(II) catalysts were  $\text{PdCl}_2(\text{PPh}_3)_2$  and  $\text{PdCl}_2(\text{PhCN})_2$ .

In contrast to the cyclic disilane reactions reported by Sakurai, the addition of difluorodisilanes to 1,3-dienes proceeded smoothly, with both  $\text{PdCl}_2(\text{PPh}_3)_2$  and  $\text{Pd}(\text{PPh}_3)_4$  at 100 °C, to give predominantly (43–97%), the 1:1 adducts **29**.<sup>24</sup>



$\text{R} = \text{Ph or Me}$

No steric inhibition of the reaction was observed when a competitive reaction was run between isoprene and 2,3-dimethyl-1,3-butadiene. The 1,4 addition was found to be stereoselective with only the (*Z*) isomers of **29** being formed analogous to the addition of disilanes to acetylenes, *vide supra*. When 1:2 adducts **30** were produced, they were a mixture of *cis* and *trans* isomers, although a regioselective head-to-head coupling of the dienes was still found.

Chlorodisilanes have also been found to add to 1,3-butadienes at temperatures between 60 and 130 °C when catalyzed by both Pd(0) and Pd(II) complexes (eq 13).<sup>25</sup>

